

# **Preparation of a Polylactic Acid with Hydroxyapatite Reinforcement Composite**

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By

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## Approval Page

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## Abstract

Biodegradable polymers are a prime material choice for temporary biomedical devices due to its ability to degrade into non-toxic products for their use *in vivo*. However, polylactic acid (PLA) by itself lacks the sufficient strength and stiffness to permit their use as its properties begin to decrease as the polymer degrades. To improve the polymer's mechanical properties, hydroxyapatite (HA) will be added to the PLA solution to act as reinforcement. The chemical property, glass transition temperature of a polymer, also plays a key role in the mechanical properties of the polymer. PLA's glass temperature is 130°F. A polymer that is cured at a temperature below the glass temperature is found to be brittle. But at a temperature above the glass temperature, the material is found to be ductile. For the intention of using the composite material for a temporary medical device, a material with ductile characteristics is preferred. Preparation of the composite first involved the degradation of the PLA pellets given by the company NatureWorks. 1.50 grams of PLA pellets and dimethylformamide (DMF) are mixed for about 30 minutes at a temperature of 170°F to degrade the pellets. Once the pellets are fully dissolved in the solvent, HA was added to the solution. 15 minutes were given for each sample to provide a homogenous mixture. Once mixed the solution was carefully casted onto a glass slide that was set on top of another hot plate pre-heated to a temperature above the glass temperature. The final stage of preparing the composite is obtaining a composite thin film. An amount of HA added to the solution was varied for each test. It was observed that a small amount of HA is preferred due to less formation of bubbles found on the surface as the sample fully cures. Bubbles become stress concentrators, which creates a brittle material.

## Key Words

Materials Engineering, polylactic acid, PLA, hydroxyapatite, HA, degradation, curing, films

# Introduction

## Problem Statement

Polymers are weak. An addition of another material to the polymer will create a stronger polymer composite. For this project, HA was added to the PLA solution as a reinforcement. A study of varying amounts of hydroxyapatite for each test was conducted and analyzed. With a stronger composite provided for temporary medical devices, the application can withstand more force along with providing support for a longer period of time.

## Background

### Biomaterials

A biomaterial is a material “intended to interface with biological systems to evaluate, treat, augment, or replace any tissue, organ or function of the body.”<sup>1</sup> It can safely interact within the body, making the material biocompatible. Biomaterials range from metals, ceramics, and polymers (**Figure 1**). This project’s focus will be on the two main components of the project, the polylactic acid (PLA) and hydroxyapatite (HA), which are a polymer and a ceramic (respectively).



Figure 1. Biocompatible screw implants made out of a polymer, ceramic, and metal (left to right).<sup>2</sup>



## History of Biomaterials

The first known used biomaterial was during the Egyptian time (around 200 A.D.) where linen was used as a suture material. It wasn't until World War II's aftermath of heavy casualties that significantly drove the development of biomaterials.<sup>3</sup> It was estimated that the market size of biomaterials is over \$9 billion per year to date.<sup>1</sup> The most common medical devices made are of replacement heart valves, synthetic vascular grafts, hip and knee replacements, and heart-lung machines.

Today, engineers and scientist have made advances in the biomaterial world such as a "smart" material made to help guide the biological response to the implant area and an injectable material that can be applied locally without any pain. The future of biomaterials is said to rely on the "detail knowledge of cell and molecular biology and genetics"<sup>1</sup>, where the next generation of devices and implants can possibly be designed to be fully integrated into the body and cause reproduction of damaged tissue. Biomaterials are considerably new to the medical field and still developing.

## Approval of a Biomaterial

Before any material can be used within the body, it must go through many *in vitro* and *in vivo* biocompatibility tests. These tests are dictated and analyzed by agencies such as the ASTM International (ASTM). When biomaterials are ready to be sold in the market, they must be approved by the U.S. Food and Drug Administration (FDA). The FDA will be given the results from the biocompatibility test, and then analyzed the test to see if the new device is both safe and effective. Since this project is intended for a biodegradable implant, more *in vivo* test are desired.

ASTM standards used for this project are covered under the "Design and Processing" section.

## Broader Impacts

### *Manufacturability*

Polymers are processed and manufactured in many ways such as injection molding and compression molding. However, the equipment used to treat polymers was not available for this project. Melting the PLA at its melting temperature of 336°F was suggested not to be done because at these high temperatures, the surface of the PLA begins to char. Charring of the surface would produce false mechanical data. The best way to process and manufacture this composite was to degrade the PLA with the use of a solvent, and then cured the solution using only a hot plate, which was one of the equipment readily available.

### Health and Safety

One of the concerns with biomaterial implants today is the surgery involving the removal of the implant from the body. With a second surgery, it is more likely for complications to occur, which can lead to serious effects. LASIK eye surgeons reported that laser eye surgery complications occur below one percent.<sup>4</sup> However, any time you expose the body to the atmosphere can become a serious problem when the environment is not sterile. Surgery occurring close to vital organs, such as the brain or the spinal cord, increases the likelihood of complications from occurring since these areas are sensitive.

## The Biomaterial: Polymer

A polymer is made up of long chains of atoms connected by directional, covalent bonds. The building blocks of a polymer is called a mer, which is a repeated structure found in the chemical structure (**Figure 2**). In general, polymers are of a high interest material in the medical field due to its range of physical and chemical properties. One particular property is the ability to degrade within the body into non-toxic chemicals that can be easily flushed out of the body. This type of polymer is called a biodegradable polymer. An example of a biodegradable polymer is polylactic acid.

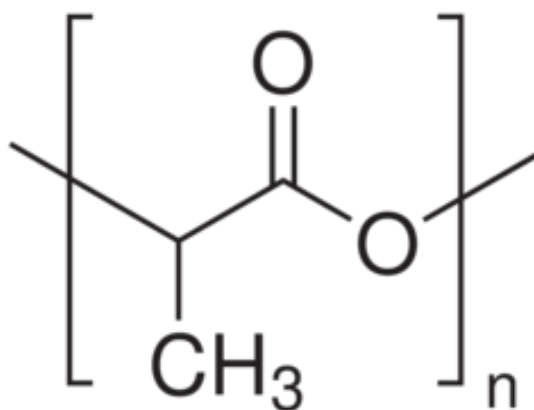


Figure 2. The mer unit of PLA.<sup>5</sup>

### Polylactic Acid

Polylactic acid (PLA) is a biodegradable polymer that is commonly used in medical applications such as sutures (**Figure 1**). It is a rigid thermoplastic polymer made from fermented corn. PLA has unique properties such as the “ability to stress crystallized, thermally crystallized, impact modified, filled, copolymerized, and processed in most polymer processing equipment.”<sup>6</sup>



Figure 3. Biodegradable polymer fiber is used to close up a wound in order to heal.<sup>7</sup>

The product, Ingeo™ Biopolymer 3001D made from NatureWorks, was used for this project (**Table I**). This specific product is found in applications such as cutlery, cups, plates, and cosmetics. It is particularly processed by injection molding. When using this product, the moisture content of the environment must be less than 0.25% to prevent viscosity degradation. But because the application is intended to degrade, this does not pose as a problem. The problem, however, will be have fast the PLA may degrade.

Table I. Mechanical properties of the Ingeo™ Biopolymer 3001D product.<sup>8</sup>

Properties	Data
Tensile Yield Strength	62 MPa
Flexural Strength	108 MPa
Flexural Modulus	3600 MPa
Glass Temperature	130°F
Melting Temperature	336°F

### *Production of PLA*

The largest producer of lactic acid in the world is the company NatureWorks. Their factory is located in the middle of large areas of corn fields, which is the main product used to make their lactic acid. The process starts with the gathering and milling of corn kernels, where dextrose is extracted from the starch. The dextrose is then converted into lactic acid, which is a by-product of fermentation. Lactic acid is converted to lactide, where the lactide molecules will link into long chains making the polylactic acid (**Figure 4**).<sup>9</sup>

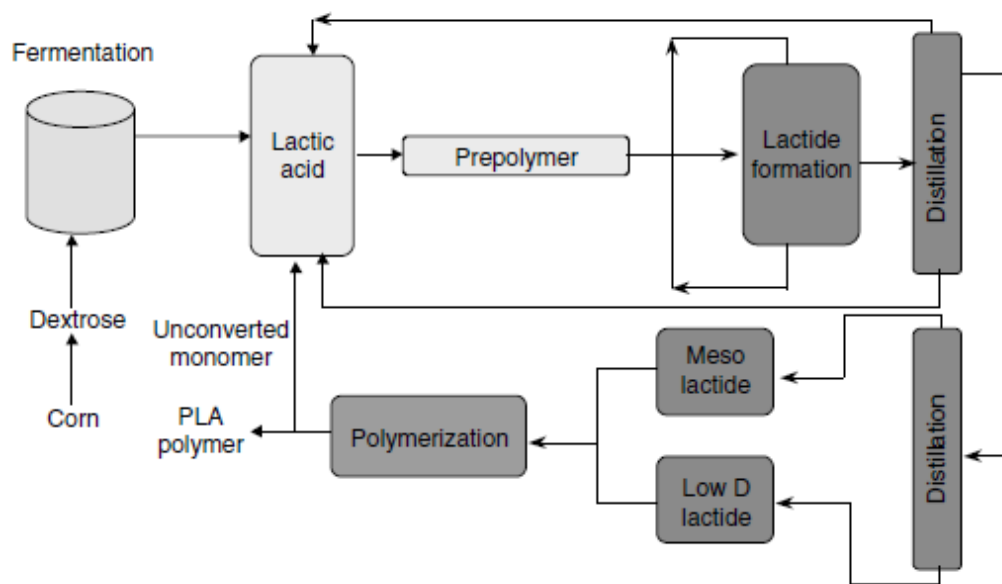


Figure 4. Schematic of the production process of PLA.<sup>6</sup>

### *Degradation Process of PLA*

When a device is inserted into the body, the body quickly reacts to the new material. It causes inflammation cells that attack the surface of the new material, and produce active substances that create a harsh environment, therefore speeding up the process of degradation. For a biodegradable device, this reaction is desired. A typical biodegradable polymer suture would degrade in 60 days, where most of its tensile strength is gone.<sup>3</sup>

There are three general mechanisms to degrade a polymer (**Figure 5**). Mechanism one is where the water-soluble bonds between the polymer chains are broken. Mechanism two involves cleaving the hydrophobic side chains and revealing the hydrophilic groups. Mechanism three attacks the backbone itself.<sup>1</sup> The degradation process can depend on a range of factors such as molecular weight, pH, crystallinity, purity, and temperature.<sup>6</sup>

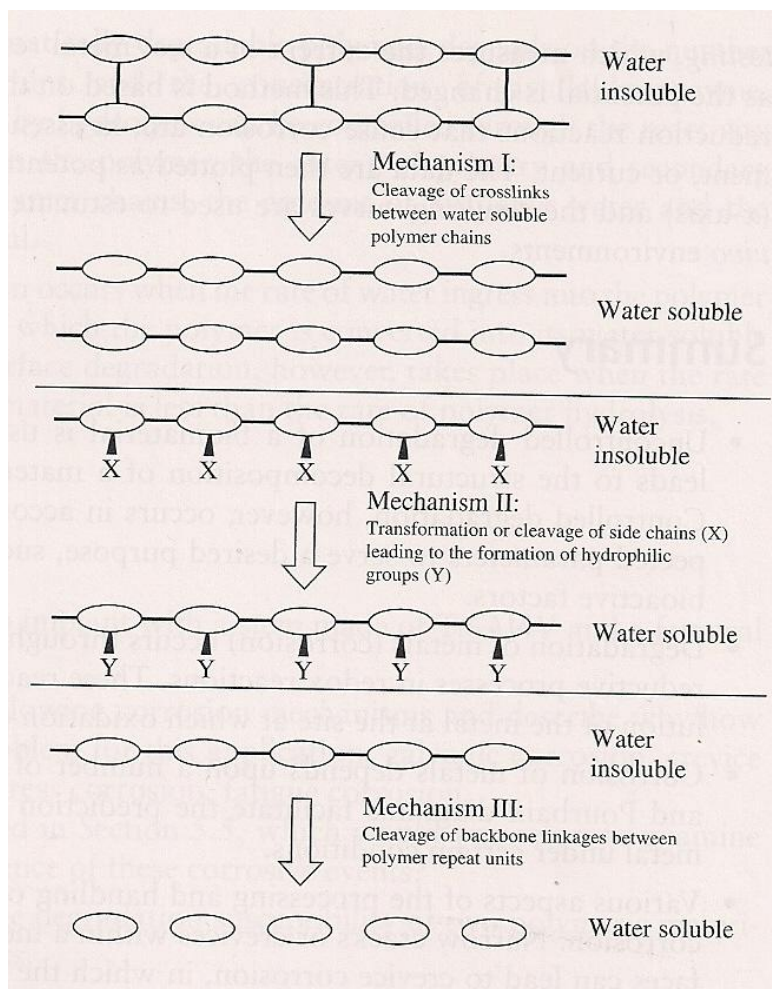


Figure 5. Three degradation mechanisms for a polymer.<sup>1</sup>

### *The Glass Transition Temperature*

The most highlighted property of a polymer would be the glass transition temperature. It is the glass transition temperature that determines the mechanical properties of a polymer. Below the glass transition temperature, the material is found to be glassy and brittle. This is because at this low temperature, the polymer chains are said to be “frozen”, where there is not enough energy to cause molecular motion. At temperatures above the glass transition temperature, polymer chains can slide past one another causing the material to be rubbery, and elastic. This is due to enough energy given to the atom to cause a molecular motion. For a temporary medical application, a ductile material is desired.

### *The Curing Process*

The curing process of a polymer is a thermally activated process.<sup>10</sup> Temperature and time play a large role in the curing process of a thermoplastic polymer.<sup>11</sup> When heated, the polymer softens and become

more fluid as heat increases. This is due to the secondary bonding between the polymer chains. Curing process for a ductile polymer occurs at a low enough temperature for secondary bonds to reform.<sup>1</sup> Curing of the composite will determine the quality and performance of the molded product.

### Viscosity

Viscosity is the “measure of a fluids resistance to flow under shear stresses”.<sup>11</sup> Fluids, such as water, have low viscosity and can flow readily. Polymer melts are also a kind of fluid, but have a high viscosity and flow only under high stresses. The two most important factors of viscosity is temperature and shear rate. A low viscosity is needed when mixing two materials in order to achieve a homogeneous mixture.

The starting material for a thermoplastic resin is a low-viscosity fluid. With an increase in cure time or temperature, the rate of viscosity increases. This pattern is seen in all cases, including thermosets **(Figure 6)**. The rate of viscosity is low at the early stage of curing. When the threshold of cure is reached, the viscosity rate increases rapidly. At the end of curing, the viscosity is high and the flow of the solution becomes increasingly difficult. But be aware that if the temperature is close to the melting temperature of PLA, the high temperatures provides enough energy for atoms to vibrate furiously breaking the bonds that hold the atoms in place.

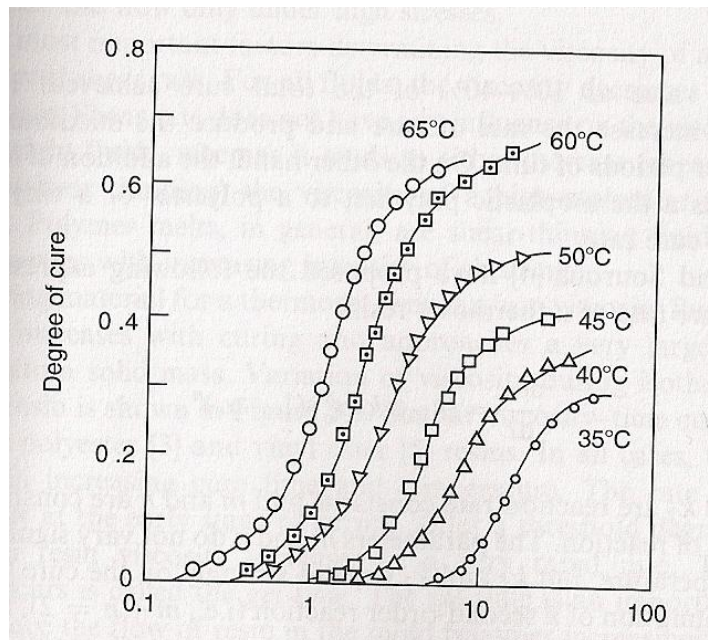


Figure 6. The degree of cure for a vinyl ester resin at various temperatures.<sup>11</sup>



## The Biomaterial: Hydroxyapatite

Hydroxyapatite (HA) is a biocompatible ceramic that is mostly used in applications that come in contact with bone. What makes HA unique is its ability to promote osseointegration.<sup>12</sup> Osseointegration encourages bone to grow onto the implant if the implant was coated with hydroxyapatite. HA was particularly chosen to be used for this project for this ability. Examples of applications that use hydroxyapatite are drug delivery devices and dental implants (**Figure 7**).

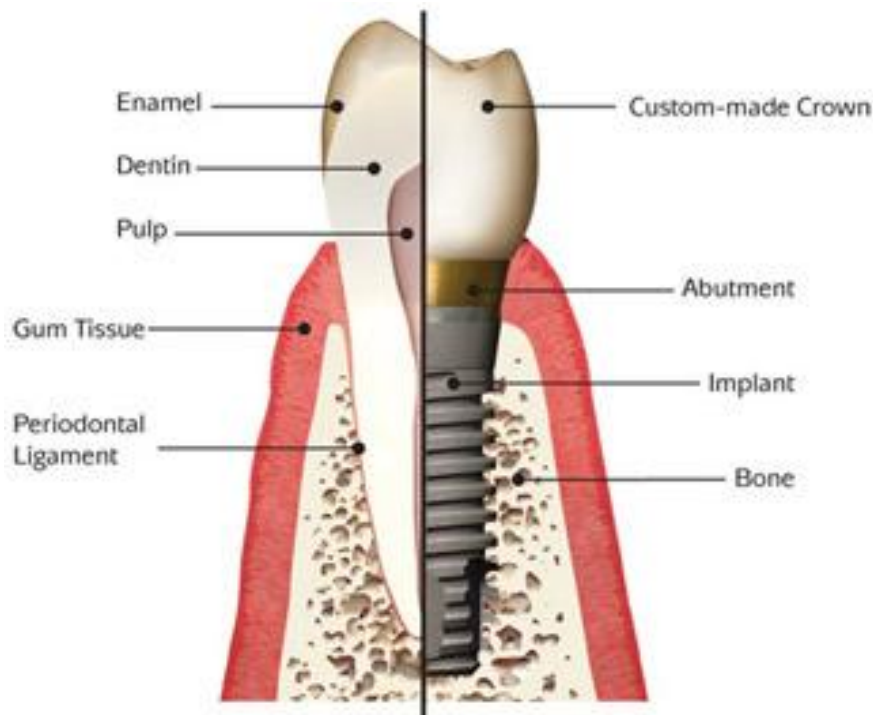


Figure 7. HA is used to make the screw implant for dental prosthesis.<sup>12</sup>

## Design and Processing

### Design Requirements

1. Composite must be biocompatible
2. Composite must be capable of fully degrading
3. Composite must be able to hold a force through numerous cycles
4. No serious side effects caused by the composite when in use
5. No failure of device within 1 year

## Design Standards

Samples produced for the project follow the standards under ASTM D882-12, ASTM D6641, and ASTM D5687 (**Table II**). However, with the lack of materials available, the number of specimens per test made were condensed from five to two. No time was available to mechanically test each sample, however, samples were prepared as if they were to be tested under the following ASTM standards.

Table II. ASTM standards used to prepare and test PLA/HA sample.

ASTM Standard	Title
D882-12	Standard Test Method for Tensile Properties of Thin Plastic Sheeting
D5687	Preparation of Flat Composite Panels with Processing Guidelines for Specimen Preparation
D6641	Compressive Properties of Polymer Matrix Composite Materials Using a Combined Loading Compression Test Fixture

## Reinforcement Selection

The addition of reinforcement within the polymer matrix was needed to create a stronger composite (**Figure 8**). Hydroxyapatite was chosen because it is biocompatible and has the ability to promote osseointegration. If this composite was used to as a material for a drug delivery device, it would allow the device to have a secure position when implanted in the body.

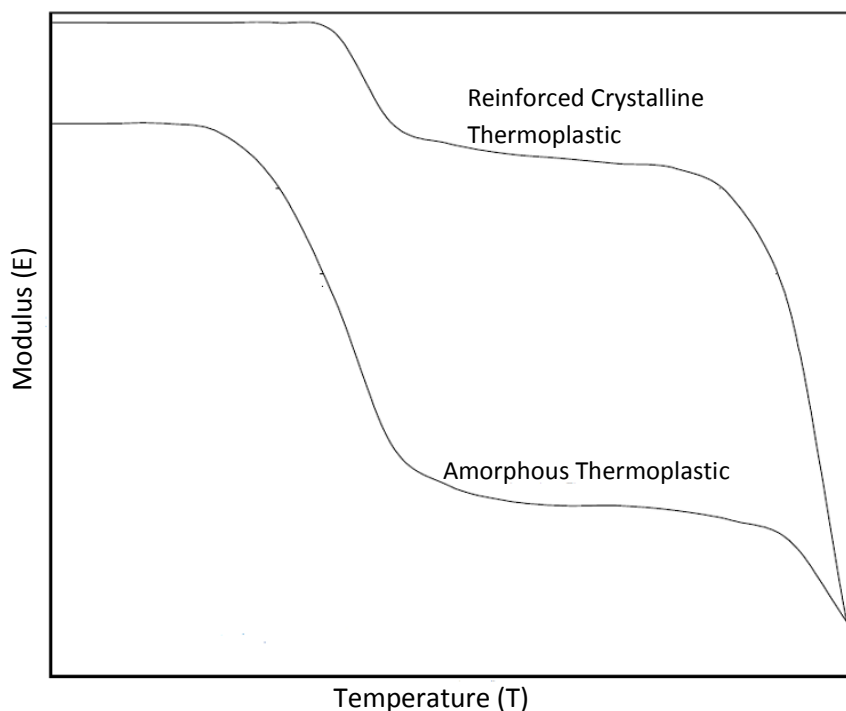


Figure 8. A comparison of the strength of a non-reinforced and reinforced polymer composite.<sup>13</sup>



## Project Apparatus

PLA and HA are the two main components of this project. 1.5 grams of PLA pellets are used for each test, which is capable of producing two samples. The amount of HA used for each test is varied. For this project, 0%, 12.5%, 37.5%, and 50.0% of HA was used. To degrade the PLA pellets, 20 milliliters of the solvent, di-methylformamide, was used. Casting of the PLA and HA solution was quickly done onto a glass slide (1x3 inches<sup>2</sup>).

The apparatus used to degrade the PLA pellets involved an electronic hot plate, a glass jar enclosed using parafilm, and a stir bar (**Figure 9**). An electronic hot plate is recommended for this part of the preparation because dealing with the PLA pellets and DMF is sensitive that it needs a specific temperature. The degradation process of PLA was done under the hood due to safety concerns of the combustible gasses DMF created at high temperatures (**Table III**).

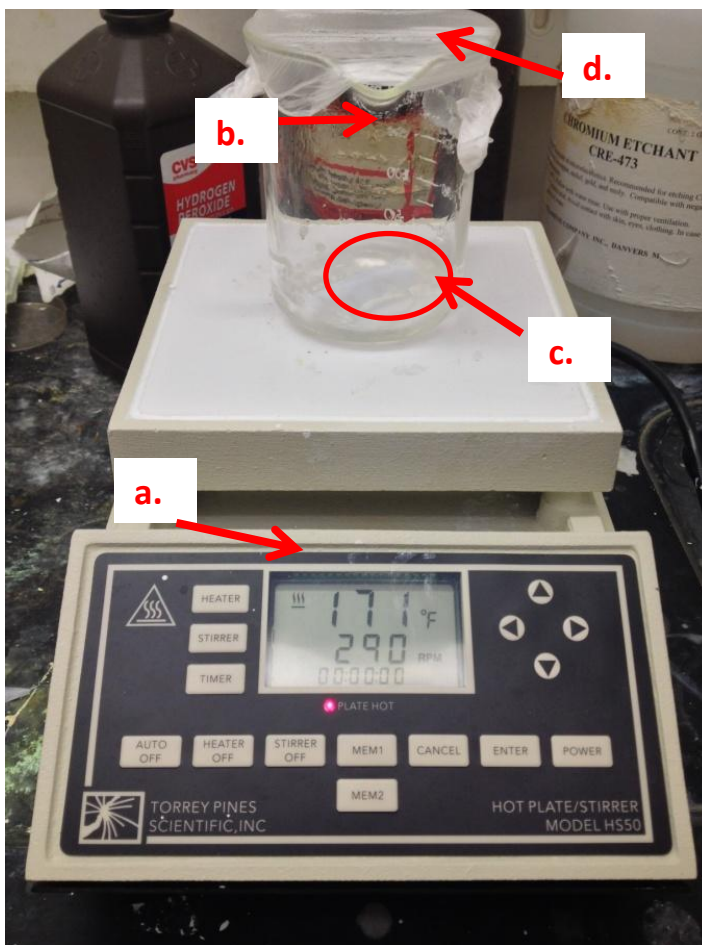


Figure 9. Apparatus used to degrade PLA pellets. (a) Electronic Hot Plate (b) Glass Jar (c) Stir Bar (d) Parafilm.

Table III. Chemical properties for the solvent dimethylformamide.<sup>14</sup>

Properties	Data
Flash Point	136.4 °F
Autoignition Temperature	833.3 °F

The apparatus used to cast the PLA and HA solution was done outside the hood in order to allow the solution sample to reach it's lowest energy state without the constant air flow of the hood. The apparatus includes a regular hot plate (**Figure 10**).

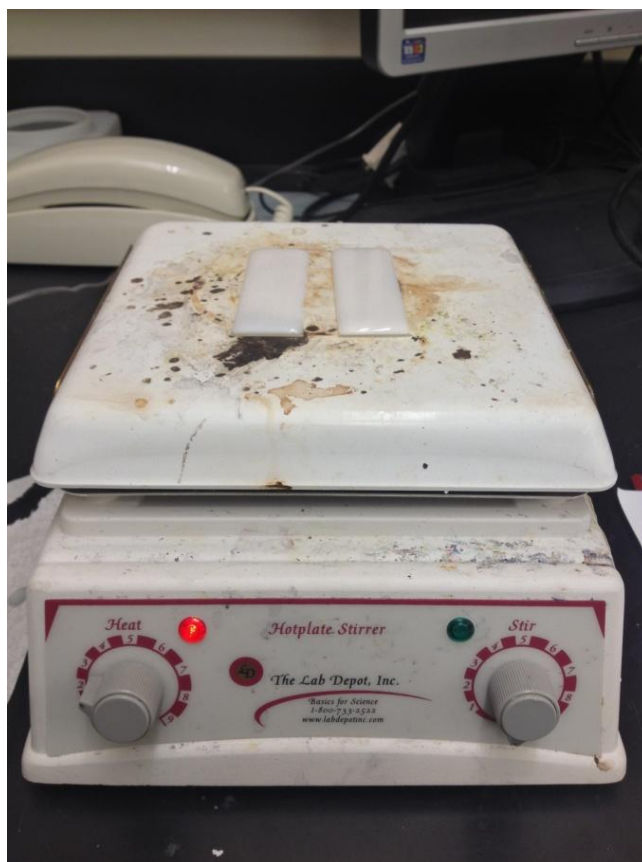


Figure 10. Apparatus used to cure the PLA/HA solution.

## Procedure

### *Degradation PLA Pellets*

For this part of the preparation process of the PLA/HA sample, it is done under the hood due to the highly combustible gasses created when the DMF is heated at a high enough temperature. A glass container is set upon the electronic hot plate. Within the glass container is the 10 milliliters of DMF used to degrade the PLA along with the stir bar. The stir bar is set into motion at 270 rounds per min (rpm),

while the hot plate is heated to a temperature of 170°F. Once the apparatus is set, 1.5 grams of PLA is added to the solution. The glass container is closed using parafilm (**Figure 9**). Degrading of the PLA pellets took about 30 minutes or until all of the pellets are fully dissolved within the solution. Constant mixing of the PLA/HA solution must occur when degrading the PLA. If the stir bar stops during the degradation process, the solution will begin to cure, making the casting part and mixing of HA into the PLA solution difficult.

Once the pellets are fully degraded, HA is added to the solution. Each test contains different amounts of PLA. The following HA percentage were used for this project: 0%, 12.5%, 37.5%, and 50.0%. In order to properly mix the HA into the PLA solution, 15 minutes were given for each test.

### *Casting of the Solution*

Before the PLA/HA solution is casted, the hot plate (regular) should be heated to the designated number of “3”. Two glass slides should be already set upon the hot plate before casting the solution. Once it is heated, the solution must be quickly and carefully poured onto the slides (**Figure 11**). This should be done in caution for the solution sometimes tend to spill outside and onto the plate itself. For best results, the stir bar should be taken out immediately before casting occurs. Extra paper towels on the side are recommended if a spilling occurs. If done accordingly, the casted solution should be fully cured in 30 minutes.



Figure 11. PLA/HA solution correctly casted onto two glass slides.

To separate the PLA/HA sample from the glass slide, set the two slides in a glass container filled with hot water. Eventually, the sample should release from the slide automatically. If this is found to be difficult, set the glass container filled with water on top of the hot plate set to a designated number of “3”, and the sample should easily pop off over time.

## Results

### The Glass Transition Temperature

A PLA sample with 0% HA was tested at temperatures below and above the glass temperature. Below the glass temperature, the samples was cured at room temperature without a hot plate. It was found that the sample was still wet after curing the PLA/HA solution for 30 minutes. The sample was left to be further cured for about three days. Once fully cured, the sample was observed to have a crack that went through the structure and appeared to be flaky (**Figure 12**). Another test was conducted, but with a sample cured at temperatures above the glass temperature. Once fully cured and separated from the glass slide, the sample was found to be flexible and strong. However, voids were found on the surface of the fully cured sample, which can affect the mechanical properties of the sample.

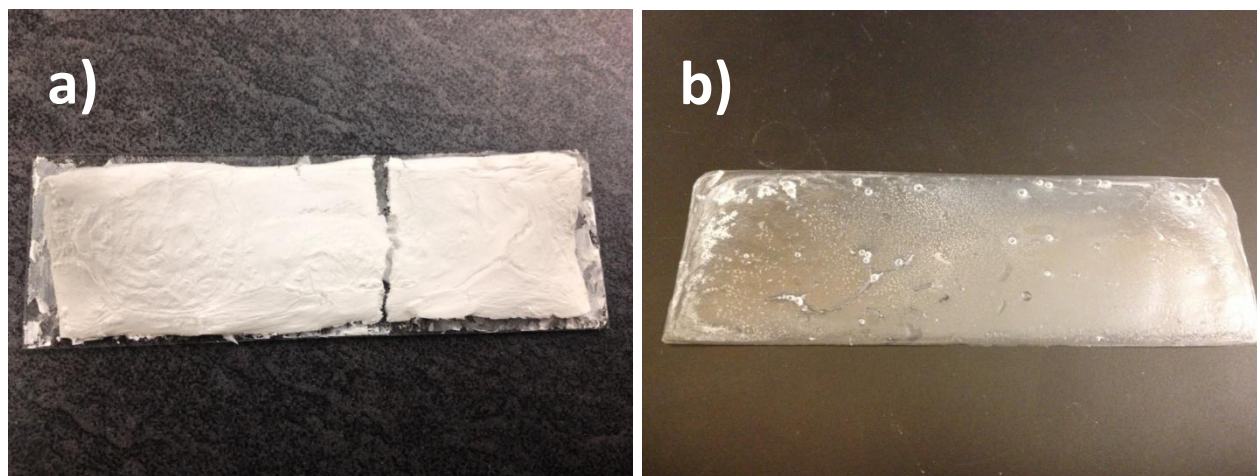


Figure 12. PLA sample cured at a temperature (a) below the glass temperature and (b) above the glass temperature.

### The Varying Amounts of Hydroxyapatite

Different amounts of HA added to the PLA solution was tested and observed. The amount tested were of 0%, 12.5%, 37.5%, and 50.0% of HA (**Figure 13**). It was observed that as the amount of HA added to

the solution increased, the more likely bubbles will be found on the surface of a fully cured sample and the more difficult it became to remove the sample from the glass slide.

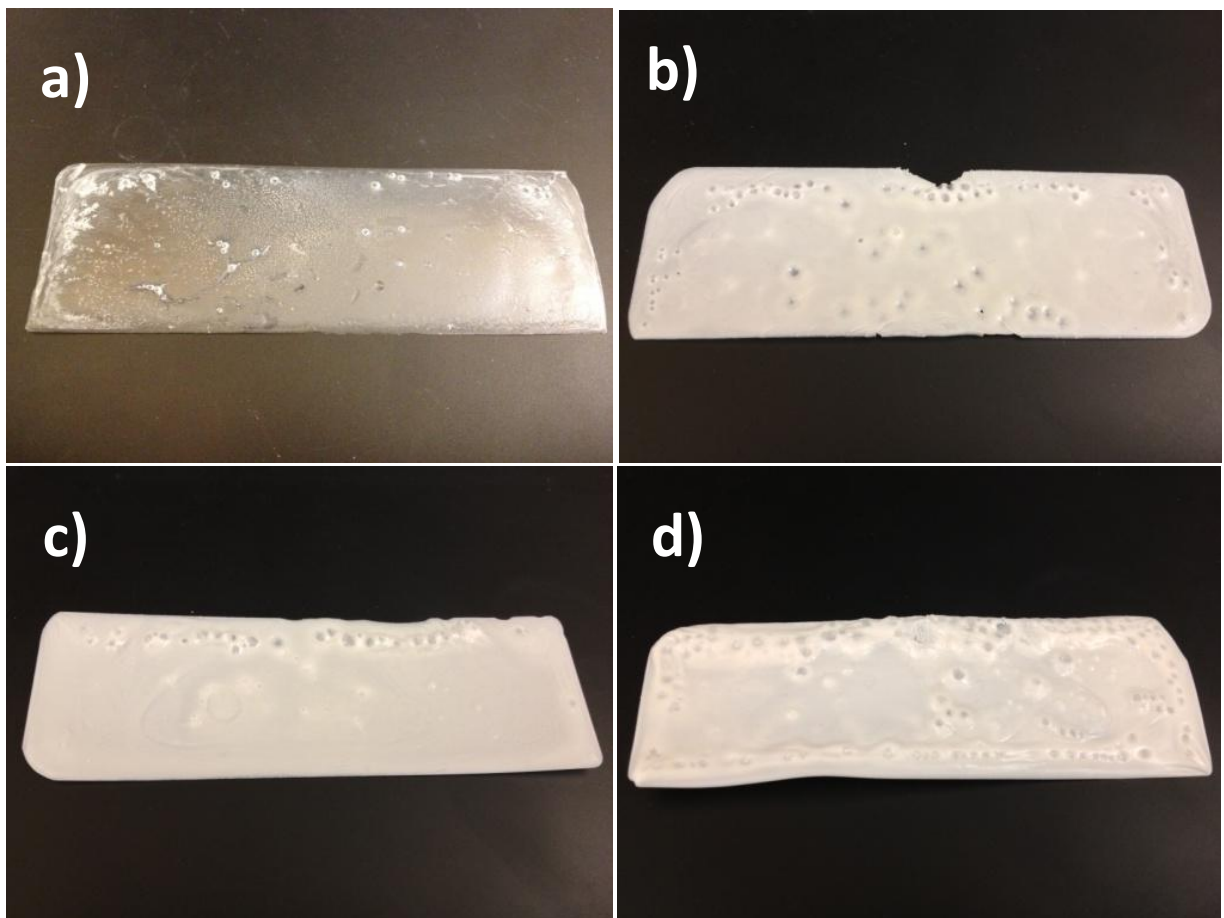


Figure 13. Amounts of (a) 0% (b) 12.5% (c) 37.5% and (d) 50% HA was added to the PLA solution and fully cured. Each sample was separated from the glass slide.

## Discussion

The glass transition temperature determined the structure of the PLA solution as researched. It was found that below the glass temperature, the material was flaky and brittle. When this sample fully cured, a crack was found to have spread through the material. This showed that a curing temperature below the glass temperature is highly undesirable. Above the glass temperature, however, showed a stronger and stiffer material. A curing temperature above the glass temperature is most desirable since it creates a ductile material that would be able to withstand a temporary load.



As the amount of HA added to the PLA solution increased, the more bubbles were found on the surface of a fully cured sample. The addition of 50% of HA to the PLA solution made the solution highly viscous. This made it extremely difficult for bubbles to escape to the atmosphere. Bubbles act as stress concentrators that would lead to a brittle material. Therefore, it is preferred that a small amount of HA is added to the solution in order to have less bubbles.

Some samples, such as the PLA solution with the 37.5%, did not follow the pattern that was discussed above. This could be due to equipment error. The hot plate used was not of best condition. It was observed that the hot plate was not of equal temperature throughout the plate and therefore would lead to inaccurate data.

## Conclusion

The following are conclusions as well as recommendations for further development for this project:

1. Preparation of a polylactic acid and hydroxyapatite reinforcement composite was proven successful with the use of a solvent and hot plate.
2. Dimethylformamide and a high temperature of 170°F is needed in order to degrade PLA pellets.
3. A curing temperature above the polymer's glass transition temperature is desirable for a temporary medical application because it produces a ductile material that can withstand a cyclic load.
4. Small amounts of HA is preferred in order to obtain less bubbles found on a fully cured PLA/HA sample.
5. Recommended to find a better temperature on the hot plate to fully cure the PLA/HA solution without bubbles.

## Future Directions

Mechanical testing of each sample could not be conducted due to the time constraint. Because the Materials Engineering Department does not have the equipment to mechanically test films, it is recommended to plan ahead and work with the Chemistry and Biology Department. Future testing should be done to find out how to remove the bubbles produced on the surface of the fully cured samples. Since the composite is intended to be used for a medical device or implant, the time it takes to degrade the film should be tested. Films should be tested in a solution with a pH level close to the body such as Hank's Balanced Salt Solution.

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